

It is likely that the stabilization and golden rule procedure can be readily applied to vibrational Feshbach resonances as well. Eastes and Marcus have successfully used the stabilization method to locate such resonances in atom-diatom oscillator colinear collisions,³⁵ although they made no attempt to evaluate the resonance widths. Location of resonances by performing scattering calculations proved in the case (narrow resonances) treated in ref 35 to be very difficult. This again supports our belief that the present L^2 method will be useful in supplementing conventional scattering techniques.

Considering our results on the model two-open-channel problem as well as work of Winkler and Yaris³¹ it seems that the stabilization procedure provides a good starting point for a more efficient, less time-consuming version of

the coordinate rotation technique. Subspaces of stabilization eigenvectors, selected via second-order perturbation theory, allow for significant reduction in the dimensionality of the complex symmetric matrices to be diagonalized in the course of computing θ trajectories. This saving may be particularly important for many-open-channel problems where the matrix dimensions can quickly become prohibitively large. The results obtained via this scheme compare favorably with full coordinate rotation results. Accounting for the neglected part the stabilization eigenvector spectrum by second-order perturbation theory does not seem worthwhile in light of our results.

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Stochastic Calculation of Interaction Energies

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A Monte Carlo method by which the properties of a collection of interacting nuclei and electrons might be accurately calculated is briefly outlined. This method allows quantitative determination of the pairwise intermolecular potential and potential surfaces but eliminates the use of these constructs for dense systems. Preliminary results on the electron gas, hydrogen solid, and the molecules He_2 , LiH , Li_2 , and H_2O are at least as accurate as the best previous work.

Introduction

Great progress has been made in recent years in quantitatively calculating the equilibrium properties of bulk matter just from knowledge of the interactions of the constituent atoms or molecules, provided these behave classically. This has been made possible through the Monte Carlo method, carried out on computers.¹ This method overcomes the mathematical difficulty of evaluating high-dimensional integrals, such as the partition function, by sampling configurations of the system, chosen according to their Boltzmann weight. The desired integral averages over these configurations are readily carried out for any property. The accuracy of the result for a given number of particles is only limited by the number of configurational averages that are practical to perform.

Very complex systems, such as long hydrocarbons and polymer fluids, have been simulated in this way, using simplified model intermolecular potentials. Although in these complex systems it is very time consuming to move from one configuration to another, the true limitation in the quantitative comparison to experiments rests in the need for accurate knowledge of the intermolecular potential. This is true even for the simplest known liquids—namely, those of the rare gases. The intermolecular po-

tential, which is the only input required in these calculations, is usually derived empirically from low-density data. Such data as transport coefficients and second virial coefficients are most commonly used, because this information can be readily inverted to yield an intermolecular pair potential. Further, very useful information about the pair potential can be derived from spectroscopic and molecular beam experiments. The best pair potential deduced from all these experiments, however, fails to quantitatively predict the dense fluid properties even for argon.² This is because the total potential is not accurately represented by the sum of pairwise potentials thus derived. Very little is known about higher-order corrections to the pairwise additive potential. Somewhat surprisingly, however, when the asymptotic triplet correction is added, in the case of the rare gases, most fluid properties are nearly quantitatively predicted.

Nevertheless, this is not a satisfactory situation from the statistical-mechanical point of view. First of all, in the process of obtaining the intermolecular potential, the statistical mechanical expressions valid at low density are utilized. This logic deprives us of any hope of calculating low-density properties from first principles. Secondly, the inversion process by which the intermolecular potential is derived is not unique. Furthermore, the interaction of

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two hydrogen molecules is impossible to determine accurately at all relative angles and separations, for example, from the limited low-density experimental information. Finally, the pair potential at low density differs by more than 10% from the effective pair potential valid at high density, even for the rare gases. Thus quantitative, a priori, prediction of high-density properties is not possible, and one is forced to invert the high-density data, to gain information on the interaction potential in this regime as well.

In the case of interaction between two different molecules, i.e., to predict the properties of their mixtures, the situation is even worse. It is becoming increasingly clear from low-density spectroscopic work on van der Waals complexes³ that the interaction potential between two different species is not chemically saturated. This means that weak, angular specific, chemical forces determine the low-density configuration of the binary complexes. Even for like species this is often the case. This leads to serious consequences. First, no general features of the intermolecular potential between different pairs of molecules can be established. Thus each given pair must be specifically studied (in general, such a system can only be considered as an interacting collection of nuclei and electrons). Furthermore, nonchemically saturated potentials cannot even be semiquantitatively considered as pairwise additive at high density. Finally, the excess properties of mixing of two different fluids are dominated by these intermolecular effects. This is because the calculation of the excess properties, being determined by a *difference* in energy between that of the mixture and the pure components, requires from one to two orders of magnitude greater precision in knowledge of the potentials than in the pure case. Thus, the quantitative prediction of the excess properties of mixing of even two rare gas fluids is not possible until a much more accurate knowledge of their mutual interaction potential at liquid densities becomes available.⁴

In the face of this situation, the concept of an intermolecular potential loses much of its value. From the theoretical point of view, calculating the intermolecular potential is no different from calculating the internal energy of an interacting many-body system. By means of the intermolecular potential concept, the problem of calculating the total internal energy has been broken up into two parts. One part consists of obtaining the interaction between two isolated entities (molecules) which are strongly bound internally but weakly interacting among themselves, usually within the Born–Oppenheimer approximation in which the nuclei are held fixed, and, the other, of obtaining the internal energy of the separate entities. This division leads to some of the above difficulties. Furthermore, even if one wants to introduce the concept of an intermolecular potential, it would be highly desirable to calculate it from first principles, rather than depend on empirical deduction of it, even if the latter were accurately possible. As we will see later, faced with the task of accurate calculation of the intermolecular potential of, let us say, two hydrogen molecules, it does not appear much more difficult to calculate the interaction of about 10 such molecules by the same techniques.⁵ From that point of view the introduction of an intermolecular potential can be eliminated.

The problem of calculating the intermolecular potential of even two hydrogen molecules, let alone 10, to the pre-

cision required is immense, but not insurmountable. What is required, of course, is the ground-state solution of a quantum many-body problem, starting from electrons and nuclei interacting with the Coulomb potential. At least *that* interparticle potential is accurately known, and spherically symmetric. The latter advantage is not inconsiderable. It might well turn out eventually, that the fully quantum mechanical calculation of the properties of 100 protons and 100 electrons to a given accuracy might be no more time consuming than the calculation of about 50 classically behaving hydrogen molecules, interacting through a complex, angular-dependent potential. The quantum calculation, even if it were slower, has the advantage of avoiding the Born–Oppenheimer and the pairwise additive potential approximations. In addition, under many conditions, hydrogen must be treated as a quantum mechanical system anyway. To be sure, hydrogen is a particularly favorable example for which to eliminate the intermediate step of an intermolecular potential. Progress in the quantitative understanding of water requires a similar approach, since its angular-dependent potential is not pairwise additive, and the hydrogen bond needs quantum mechanical treatment. To extend such calculations to finite temperatures and to excited states presents no conceptual difficulties.

The quantum many-body methods used in the past have not been of sufficient accuracy to predict well either intermolecular potentials or internal energies. The primary method that has been used for such calculations is a variational technique, in which one expands the wave function in one electron states (orbitals). These are usually taken to be of a Gaussian form, in order that the multi-center integrals may be done analytically. The calculation in its most advanced form is called configuration interaction (CI).⁶ Unfortunately this method has proved to be very slowly converging. As elaborate a calculation as is practical on the most advanced computers has not as yet led to the precision required for quantitative predictions of the interactions involved in the weak chemical complexes discussed earlier. One must therefore search for an alternative method. This will be described in the next section. The final section will discuss the preliminary results obtained so far.

Method

The proposed method by which the quantum many-body problem might be solved to sufficient precision has some of the same features as the classical many-body Monte Carlo procedure. All efforts to do the problems analytically are abandoned. The method utilizes a numerical scheme that computers can do particularly well and fast, namely a highly repetitive, simple, stochastic process. Another feature in common with the classical analogue is the introduction of importance sampling. In the classical situation this takes the form of not sampling all of phase space equally, but rather weighting by the Boltzmann factor. This procedure concentrates the calculation in the region of phase space that matters. Importance sampling is also essential to achieve a high degree of precision in the quantum calculation.⁷

The question of precision in Monte Carlo calculations appears, at first sight, to render this approach hopeless for the calculation of the intermolecular potential. Given the speed of even the fastest machine, the number of random

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moves that can be made in an hour, for example, is such that it is only possible, in the classical calculation, to obtain the internal energy to an accuracy of about 1 part in 10^3 . In the quantum case, however, the intermolecular potential typically represents a much smaller fraction of the total energy of the system than that; in the case of H_2 or He, it is of the order of 1 part in 10^5 . Thus, if one wants to calculate that potential reasonably accurately, say to 1% accuracy, a precision of 1 part in 10^7 in the energy is required. This is achievable, however. In a quantum calculation, crudely speaking, the accuracy of the Monte Carlo calculation is 1% (and in an extensive calculation perhaps 0.1%) relative to the accuracy of the importance function. Thus a high premium must be placed on an accurate and concise importance function, as will be seen. The conciseness requirement derives from the fact that values of the importance function must be frequently calculated, and this is time consuming unless the function is compact.

In fact, the importance function itself is frequently derived from a variational Monte Carlo method which is in a one-to-one correspondence with the classical Monte Carlo method.⁸ This variational procedure, in itself, is potentially more accurate than the configuration interaction procedure used primarily heretofore, since it has fewer limitations. The variational Monte Carlo procedure rests on the simple observation that the wave function—written as a pair-product wave function of the Bijl–Jastrow–Slater form—times its complex conjugate is a probability, like the Boltzmann factor. This becomes clearer if the squared product wave function is rewritten in the form of an exponential of a pairwise additive quantity, the pseudopotential. Thus, the standard classical Monte Carlo game is played, using as an interaction between the particles this pseudopotential. For fermions, to account for statistics, the wave function must also contain a Slater determinant of single particle orbitals. One can regard the logarithm of the square of the determinant as the exchange contribution to the pseudopotential. The wave function might contain a number of parameters, with respect to which the energy can be minimized. Such a variational calculation incorporates pair correlations which are left out, for example, in Hartree–Fock orbital calculations. Furthermore, triplet and higher-order correlations can be included in such calculations, if one is willing to deal with triplet and higher order pseudopotentials. This has been done, up to now, only in special cases. An additional advantage of these calculations is that they perform the high-dimensional integrals by the Monte Carlo procedure, and thus do not restrict the form of the pseudopotential—the pairwise wave function—in any significant way.

One might then ask why this variational Monte Carlo method has not been more widely used, since in the few cases that it has been tried, it leads to quite respectable results. The answer appears to be twofold. First, it seems difficult to extend the variational wave function in a systematic way, to converge as accurately as desired to the exact result. But perhaps more importantly, given that we use a Monte Carlo procedure already, further stochastic methods can improve the results by a generally valid procedure that is independent of any functional representation of the wave function. This procedure will be described next.

The Schrödinger equation can be viewed in analogy to a Fick's law diffusion process in a space of dimension three times the number of particles.⁹ The diffusion process corresponds to the kinetic energy term in the Schrödinger

equation, the diffusion coefficient given by $\hbar^2/2m$, and the wave function playing the role of the density. The other term in the Schrödinger equation, the potential energy times the wave function, can be interpreted as a "branching" term that has a probability of increasing the density per unit time proportional to the density times the potential energy. Because of this term in the quantum Monte Carlo simulation, one usually works with an ensemble of systems. Then, branching means either duplicating one of the systems in the ensemble or eliminating it. If the zero of potential energy is set to the ground-state energy, the population of the ensemble will be stable and a steady-state solution has been found. If a system is in a high- (low-) energy region, it is eliminated (duplicated) with a probability given by the exponential of the energy times the diffusion step. In this way the correct distribution corresponding to the wave function is built up. One starts out typically with about 100 members in the initial ensemble generated by the variational Monte Carlo procedure, and adjusts the ground-state energy so that the steady-state population stays near 100.

An importance function needs to be introduced, among other reasons, to avoid difficulties with singularities in the potential, and consequently in the wave function. If it were not introduced, once a positive and a negative charge had diffused close to each other, for example, the branching process would explode, corresponding to the high probability density in that region. The importance function already incorporates such singularities, and as much else as is known about the wave function, in guiding the diffusion. The Monte Carlo process only needs to correct this importance function where it is not accurate. Hence the accuracy ultimately achieved is relative to the accuracy of the importance function.

The importance function is introduced by multiplying the Schrödinger equation by it. The resulting equation is rearranged to be a diffusion equation for a density now given by the product of the importance function and the wave function.¹⁰ This rearranged equation corresponds to a slightly modified diffusion process from that discussed above. The introduction of the importance function has the significant effect that the branching process now depends on a new quantity: the difference between the local energy of the importance function evaluated at a given point in configuration space and the sought-after ground-state energy. Branching is now much reduced, and if the importance function were exact, branching would vanish. The other effect of importance sampling is that the rearranged equation contains an additional drift term, whose effect is to force the stochastic process away from regions where the wave function is small. This is obviously desirable, since in that way the process is concentrated in regions which are important.

The method, as described so far, has been successfully used to calculate properties for systems of Boson particles in the ground state.¹⁰ These are systems where the wave function is always positive. It can also be used for fermions, provided the diffusion is confined to a region where the wave function is of one sign, that is, within a region defined by the nodal surfaces.¹¹ We achieve this by adding a further constraint to the stochastic process, namely, the requirement that a system be eliminated from the ensemble once it reaches a surface where the importance function vanishes. The nodal surface is predetermined by the determinant in the importance function; for fermions the

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importance function is of the pair product wave function form multiplied by a Slater determinant. It appears, from results given in the next section, that an approximately correct location for the nodal surface leads to quite accurate results. The physical reason for this is possibly that, since the wave function is small near a node anyway, its precise location is not of great quantitative consequence. In any case, the fixed node calculation represents an upper bound to the correct answer.¹²

Nevertheless, for the high accuracy required here, the stochastic process must correct for the proper nodal surface location. The numerical process for doing so ultimately becomes unstable, because any nodal crossings at all allow the system to relax to a lower energy state (the Boson state), where there are no nodes. In spite of this instability, it has been possible to project out the fermi ground state and obtain accurate energies.¹¹ This is done by allowing systems to cross the nodal surfaces, and changing the "sign" associated with the corresponding system whenever this occurs. In this way a positive and negative population is built up, each of which relaxes to the Boson energy, but their difference rigorously leads to the ground-state Fermi energy. In the future, a more stable nodal relaxation scheme will have to be developed. One such scheme might diminish the explosive growth of the separate positive and negative populations by letting them annihilate each other if they, or their permutations, are at nearby locations in configuration space.

The error in the calculations becomes particularly evident in the nodal relaxation process. This is because the wave function is small near the nodes, and the drift force driving the system to more probable regions is hence particularly large. In that case the finite time step introduced in the diffusion process must be particularly small to avoid introducing numerical inaccuracy in solving the differential Schrödinger equation by the above difference method. To avoid such numerical inaccuracies entirely, which is highly desirable in any accurate calculations, one can go to an integral formulation of the Schrödinger equation, and solve it through a Green's function Monte Carlo (GFMC) approach. This eliminates the approximation due to the finite step size. GFMC has already been implemented for Boson systems.¹⁰ Preliminary results on Fermi systems suggest GFMC methods are more efficient for high-accuracy calculations on molecular systems.

Results

Given the preliminary state of these calculations, it is only possible to give some evidence that this approach has the potential to achieve the desired accuracy. The most extensive work has been done on the homogenous electron gas.¹¹ This calculation involves typically about 100 electrons in a box with periodic boundary conditions. This demonstrates that this scheme has no difficulty dealing with on the order of hundreds of fermions. For a typical electron density encountered in the conduction band in a metal, the variational Monte Carlo scheme calculates the total energy correct to within 1% while the Hartree-Fock energy fails by 10%. The fixed-node diffusion calculation betters the variational Monte Carlo result by another order of magnitude. Finally, relaxing the nodes leads to an estimate whose error is still an order of magnitude lower. Thus the full stochastic method improves the importance sampling variational wave function result by two orders of magnitude, achieving an accuracy of 1 part in 10^4 in the

energy. This is an absolute energy error of about 10 K per particle. Although one would have to run 100 times longer to achieve 1 K accuracy, that might be feasible with the next generation of fast computers, using an optimized program. One could also improve the accuracy of the importance wave function by an order of magnitude to achieve this accuracy. This is difficult, but probably attainable. However, a combination of longer runs and improved importance functions brings the possibility of 1 K accuracy into the present.

The 1 K accuracy level is also what one would like to obtain for the solid molecular hydrogen system, whose pair potential has a maximum depth of about 30 K. However, this is more difficult to achieve because of the inhomogeneity introduced by the protonic potential. The present variational Monte Carlo calculations are not yet as accurate as that of the electron gas although they may be improved by using more elaborate pseudopotentials. Currently, the fixed node calculations have an error of about 100 K per atom.⁵ Releasing the nodes is not likely to change that result very much, since in molecular hydrogen the electrons are bound, or localized. The wave function is hence small anyway, in the region where the nodes might be located. Small errors in nodal locations should thus lead to much less significant energy lowering than in the case of the electron gas. This, however, has not as yet been verified. Within the present accuracy, it has, nevertheless, been possible to make accurate calculations at high densities, where the repulsive pair intermolecular potential would be larger than 100 K. The calculated pressure at conditions corresponding to 50 kbar agrees with the experimentally measured one within the statistical error bars of the numerical calculation.

In molecular systems, 1 K accuracy has been achieved in the interatomic potential calculation between two helium atoms. A very accurate importance function was used,¹⁴ made by combining two (each with close to 200 parameters) isolated helium atom wave functions. Such complex importance functions are not prohibitive to use in such few electron problems. In fact, the runs so far were carried out on small computers, and longer runs on better equipment and using more accurate procedures to combine the atomic functions could well reduce the error by another order of magnitude. Thus one could reach the goal of 1% uncertainty in the maximum depth of the pair potential well. This would be significantly better than the experimental uncertainty with which that potential is now known. The quantum mechanical many-body calculation would then be in a position to make reliable predictions. The preliminary result for the maximum potential depth is 11 ± 1 K, while the experimental result is 10.5 ± 0.5 K.¹⁵ This numerical result has to be corrected for nodal release, but, as in bulk hydrogen, would not lower the energy significantly, for the Born-Oppenheimer approximation, and for relativistic effects, which are also expected to be small, especially for the difference between the interacting and isolated helium atoms. (It is worth pointing out in this connection that the quoted error bars in this calculation are absolute error bars and do not depend, as in so many previous calculations, on the accurate cancellations of correlation effects.) It is not difficult in the numerical scheme to remove the Born-Oppenheimer approximation. In fact, in the solid-hydrogen calculation that has already

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been done, by letting the protons also diffuse, but with a diffusion coefficient smaller by a factor of the ratio of the electron to proton mass.

The fixed-node calculations¹² for the potential surface of Li₂ and LiH have not yet been carried as far as for He. The best variational Monte Carlo calculation for the equilibrium configuration using either Slater or Gaussian orbitals in the determinant, multiplied by a simple Padé approximant form of the pair wave function, yields about half the correlation energy.¹³ (The correlation energy is the difference between the experimental result and the best Hartree-Fock calculation.) The subsequent fixed-node calculations brings the results, within the rather large statistical error bar of about 1000 K, into agreement with experiments. Hence longer runs need to be made to bring the error bar down, so that the effect of the incorrect nodes can be ascertained. It is, however, already clear that the fixed-node approximation calculates in excess of 95% of the correlation energy in these rather few electron systems. With respect to the accuracy of obtaining potential surfaces the possibility should be pointed out that by using a differential Monte Carlo method, potential energy differences of neighboring regions on the potential surface can probably be calculated more accurately than the absolute energies by an order of magnitude.

Finally, the preliminary results for the binding energy of a single molecule of water should be cited as repre-

sentative of what might be done for more complex molecules.¹² Again the variational Monte Carlo results can be considerably improved, since the importance functions used so far yield energies no better than the Hartree-Fock calculations. In general it is hoped that the variational Monte Carlo calculation should yield 90% of the correlation energy and the subsequent stochastic processes obtain 99.9% of the correlation energy. The fixed-node calculation for water, with a crude importance function, gives 80% of the correlation energy. The error bar is such that the remaining 20% is primarily due to the poor nodes of the importance function. Nevertheless, the accuracy of this preliminary calculation already exceeds the accuracy of the best CI calculation.¹⁶ This approach certainly represents a new direction for the theoretical quantum potential calculations, and at this stage it shows much promise.

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Ordinary Field-Theoretic Methods for Self-Consistent Wave Functions Which Describe Bond Formation and Dissociation[†]

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Three observations motivated the present work: (1) the Bardeen-Cooper-Schrieffer (BCS) wave function may be used to describe chemical bonding in formally the same way it is used to account for Cooper pairing; (2) the BCS wave function and a spinor or quasi-particle representation induce the same field-theoretic methods as the Hartree-Fock (HF) wave function and the usual second-quantization; and (3) a Lipkin Hamiltonian negates the manifest particle nonconservation of the BCS wave function. Self-consistent BCS wave functions and solution methods which are appropriate for chemical bonding are described in this paper. Orbitals are rigorously defined by even-replacement multiconfigurational Fock operators. Density distributions are defined by the Hartree-Bogoliubov equations. The Lipkin Hamiltonian is computed by successive approximations in a manner which is similar to the BCS and Nogami theories. Orbital equations which are effectively the same as the HF equations are also obtained.

1. Introduction

Self-consistent one-particle methods have proved useful for studying many-body systems. Any such method which employs a physical vacuum is amenable to the techniques of second quantization, namely, infinite order diagrammatic Feynman-Dyson perturbation, theory¹ and equations-of-motion (EOM) theory.² It is usually true that the effectively one-particle methods violate known conserva-

tion principles. Lipkin³ showed how to use vacuum wave functions which violate conservation principles. The Lipkin procedure employs model Hamiltonians, which I shall call Lipkin Hamiltonians. Self-consistent and/or field-theoretic methods may be based on the Lipkin Hamiltonians. The present work is concerned with particle nonconservation.

Hartree-Fock (HF) theory leads naturally to the particle-hole vacuum, and vice versa. This vacuum is un-

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